

A Novel Approach to Surrogate and Matrix Spiking Ambient Air Samples for EPA Methods TO-14A and TO-15

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Abstract

Surrogate and matrix spiking is a routine part of the quality control program in USEPA Methodologies for the analysis of water and soil samples. Recovery information from surrogate and matrix spiking of field samples yields valuable insight into the accuracy of the instrumental analysis and identifies possible sample matrix interactions with the target compounds. Currently, the EPA has two methods for analysis of volatile organic compounds in ambient air collected in specially prepared canisters, Methods TO-14A and TO-15. Method TO-14A has little to no QC guidance whereas Method TO-15 has more stringent criteria. However, neither method requires surrogate or matrix spiking as a part of its QC criteria. Important information about the instrumental analysis, sample matrix interactions, and sample train integrity could be derived from spiking ambient air samples.

This study was done to investigate the viability of surrogate and matrix spiking of ambient air samples collected in SilcoCans® and SUMMA® canisters, identify some of the problems, and develop a spiking procedure. For the study, the surrogate compounds include Toluene-d₈ and 1,4-Dichlorobenzene-d₄. The matrix spiking compounds are 1,1-Dichloroethene, Trichloroethene, Benzene, Toluene, and Chlorobenzene.

Introduction

The purpose of this study was to identify the feasibility of introducing a surrogate and matrix spiking procedure into the analysis of ambient air samples collected in canisters and analyzed by Method TO-14A. Surrogate and matrix spiking of field samples is a routine part of many regulatory methodologies and is useful in the evaluation of the integrity of the analytical system used in the generation of sample results. Development of a similar procedure for air sample analysis could, from a quality assurance perspective, add additional information to support results.

Our approach in the development of this procedure was to provide a quality control aspect that, based upon the recovery of spiked constituents, would duplicate the conditions a field sample might be exposed to during collection, handling, and analysis. We proposed spiking small volumes of surrogate and matrix spike material into evacuated canisters prior to sample collection in order to provide a means of replicating the conditions the field sample would be under once it was collected, shipped, and analyzed. This would allow us to identify potential issues arising from sample-canister interactions, sample loss, errors in sample preparation, or instrumental stability. The compounds chosen for the study were selected based upon compound class and availability. An effort was made to select compounds that would be representative of major compound classes found in the method compound list. This would provide information on how those classes of compounds might behave, upon collection, in field samples. Our primary

concern was to develop a reliable procedure that would allow analysts and end users to validate the integrity of the analytical system.

A multi-sample study was conducted to evaluate the spiking procedure and involved the collection of authentic ambient air samples collected from various locations in and around a commercial analytical laboratory. The sampling locations were selected in order to provide matrices of varying humidity, background, and contamination level. All samples for the study were analyzed by method TO-14A on the same analytical system. The data evaluation included absolute surrogate and matrix compound recovery, compound stability in canisters prior to collection, compound stability in canisters after collection, and reproducibility.

EXPERIMENTAL

Instrumentation and Standards

Samples were analyzed using a Nutech 3550A Concentrator with a 354A Cryfocusing accessory interfaced to an HP 5890 Series II Gas Chromatograph and HP 5971 Mass Selective Detector. A J&W Scientific DB-1 60-m x 0.32 mm ID, 1 μ m phase thickness column was used for component separation.

A gas blending system was used to generate individual calibration standards from 1-ppmv primary gas standards in high-pressure aluminum cylinder (Spectra Gases, Branchburg, NJ). The internal standards used were Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene- d_5 . The working concentration of 10 ppbv is established by the internal standard injection loop in the 3550A. Bromofluorobenzene (BFB) was added to this mix to be used for daily tuning of the mass spectrometer.

Surrogate compounds Toluene- d_8 and 1,4-Dichlorobenzene- d_4 and the matrix spiking compounds 1,1-Dichloroethene, Benzene, Toluene, Trichloroethene, and Chlorobenzene were spiked from separate 1 ppmv primary standards (Spectra Gases, Branchburg, NJ).

Canister Spiking, Collection, and Analysis

All sample canisters, (six-liter SilcoCans®, Restek Corporation, Bellefonte, PA and stainless steel SUMMA® canisters, Andersen Instruments, Smyrna, GA), were certified clean as described by U.S. EPA Method TO-14A prior to spiking and collection.

Prior to sample collection each canister, under approximately 30" Hg vacuum, was spiked with 60 milliliters of spiking standard via flow meter. From the initial concentration and the volume of the spiked added and the final volume of the canister, the final concentration of the surrogates and/or matrix spiked compounds was determined. For this study, a targeted spiked concentration of 10 ppbv for each compound was used based upon a six-liter sample volume. After sample canisters were spiked they were allowed to equilibrate for at least eight hours before sample collection. For the initial round of sampling an additional five sample canisters were spiked and set aside for long term stability testing. The ambient air samples collected during the initial round were also set aside for long term stability testing. After sample collection, the canisters were allowed to sit for at least eight hours. Before analysis, the pressure of each canister was measured and recorded to determine the final volume of each sample. At each site, four grab samples were collected, one canister spiked with surrogates, two canisters spiked with surrogates and matrix compounds, and one canister that was not spiked (parent sample) to provide background verification for the spiked canisters. Seven sites were sampled over a period of eight weeks resulting in 79 data points for surrogate recovery, and 52 data points for matrix spike and matrix spike duplicates pairs. The five canisters that were set aside to show the stability before collection were used for sampling 1, 11, 29, 36, and 55 days after spiking.

Canisters were analyzed after successful completion of the following technical acceptance criteria:

1. BFB tune (Passing criteria as stated in Method TO-15).
2. Generating a 5-point calibration curve (0.5, 5, 10, 20, 40 ppbv). After a passing curve has been established, a 10-ppbv continuing calibration verification (CCV) will be run each day after the BFB tune.
3. Laboratory Control Sample (LCS)- 10 ppbv independent calibration verification standard.
4. Blank analysis verifying that the analytical system is free of target compounds below the reporting limit of 0.5 ppbv.
5. The % RSDs must be less than or equal to 30% on the initial calibration curve. The % difference for the CCV should be <30%. The % recovery for the LCS should be 70-130%.

RESULTS

Recovery data for the surrogate compounds (Toulene-d₈, and 1,4-Dichlorobenzene-d₄) are shown in Fig 1 and Fig 2 respectively. Absolute recovery ranges for Toluene-d₈ (target concentration 10ppbv) were from 7.3 ppbv to 15.0 ppbv with an over all standard deviation of 1.5.

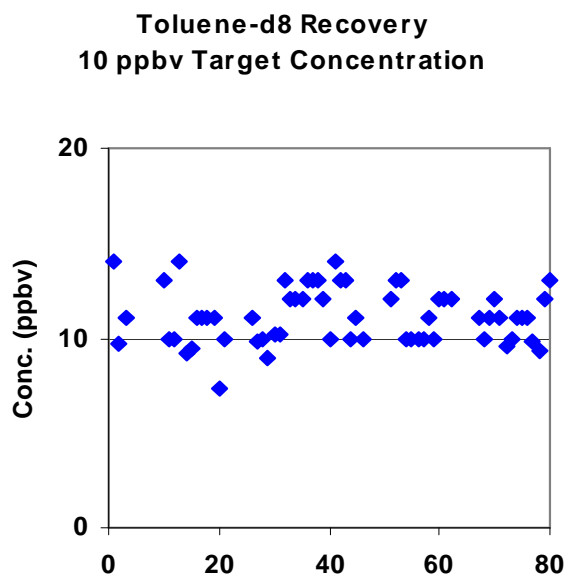


Figure 1. Toluene-d₈ Recoveries for all data points

Absolute recovery ranges for 1,4-Dichlorobenzene-d₄ (target concentration 10ppbv) were from 3.4 ppbv to 14.0 ppbv with an over all standard deviation of 2.76.

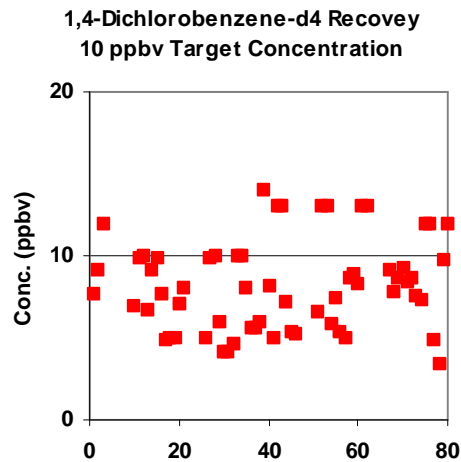


Figure 2. 1,4-Dichlorobenzene-d₄ Recoveries for all data points

Overall, Toluene-d₈ recovered very well in varying humidities and contamination levels. However, 1,4-Dichlorobenzene-d₄ was shown to be very unstable. The low recoveries happened in both low and high humidity and in Summa® and SilcoCans®.

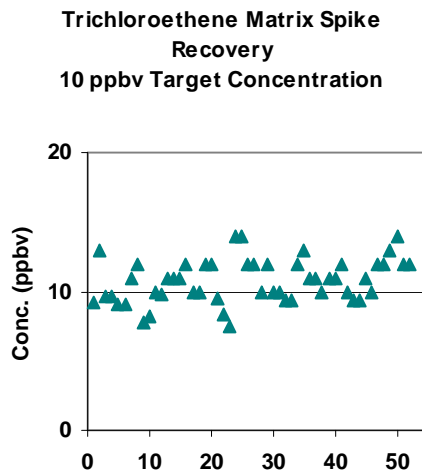


Figure 3 Typical matrix spike compound recoveries (Trichloroethene).

As an example of the matrix spike recoveries, Trichloroethene is shown above. All of the matrix spike compounds were very consistent with their recoveries. The humidity and contamination levels, as well as the canister type proved to have no effect on the results.

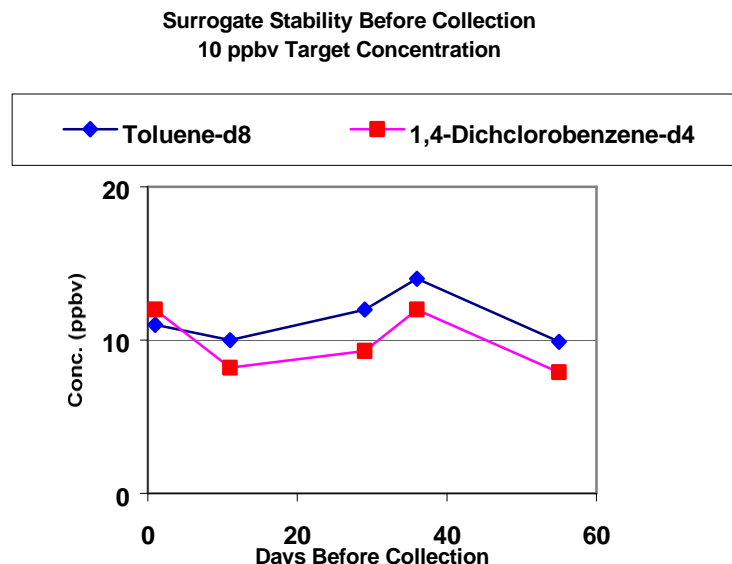


Figure 4. Surrogate Stability before Collection.

Figure 4 shows the recovery of surrogates after being allowed to sit in the canisters x number of days before collection. The data indicates that there is no significant loss of the surrogates when they are spiked in the canisters and allowed to sit for up to 55 days before collection. There appeared to be no adsorption of the spiked compounds onto the walls of the canisters when allowed to sit under vacuum for an extended period of time.

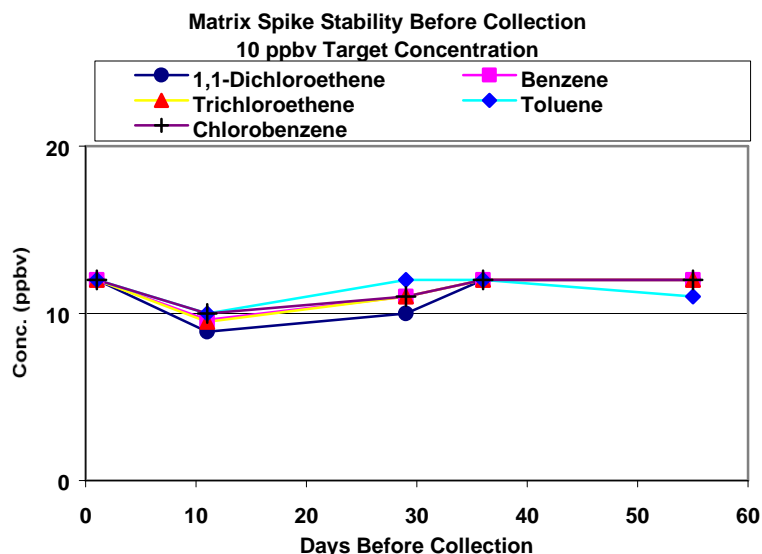


Figure 5. Matrix Spike Recoveries in cans spiked x days before collection

Figure 5 shows the recovery of the matrix spike compounds after being allowed to sit in the canisters under vacuum for x number of days. Good recovery was shown for all spiked compounds when allowed to sit under vacuum for up to 55 days before collection.

The information given in figures 4 and 5 is very valuable to us. Knowing that the compounds are stable under vacuum for up to 55 days would allow us to feel comfortable with

the analytical results even if it is a client is unable to collect a sample for a period of time after receiving the canister.

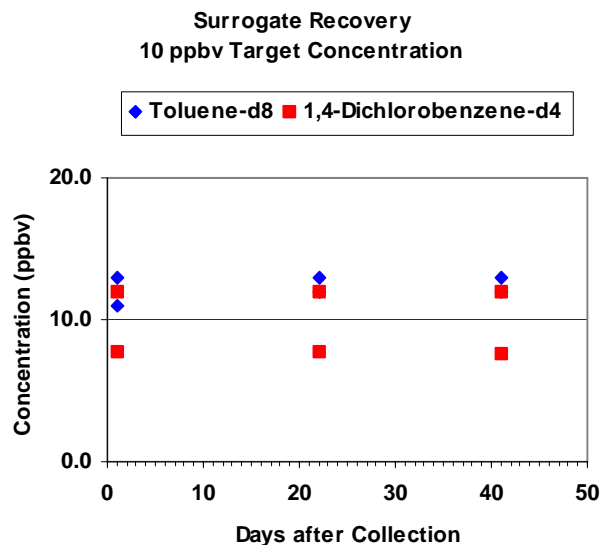


Figure 6. Surrogate stability x days after sample collection.

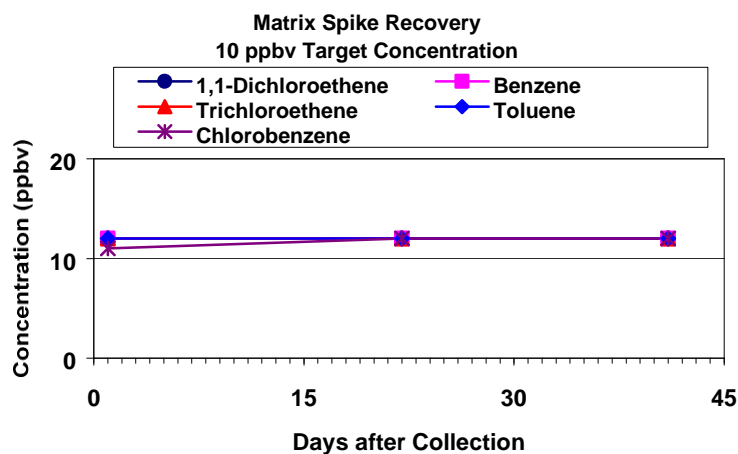


Figure 7. Matrix spike stability x days after sample collection.

Figures 6 and 7 show the stability of the spiked compounds x number of days after collection. The same canisters were analyzed days 1, 22, and 41 after collection. Surrogate and matrix spike compounds proved to be stable up to 41 days after collection. STL Burlington uses a holding time of 20 days for samples collected in canisters, so by knowing the information from figures 6 and 7, we would feel comfortable with keeping that holding time for our analyses.

CONCLUSION

Based upon the data generated from this study, it is evident that a surrogate or matrix spiking protocol may be a viable quality assurance mechanism for the analysis of ambient air sample by Methods TO-14A and TO-15. Considerations need to be made for those compounds identified for use as surrogate compounds as seen in the data from 1,4-Dichlorobenzene-d4. Where as the information from the recoveries of 1,4-Dichlorobenzene-d4 is valuable in assessing possible recoveries of like constituents (heavier weight, later eluting target compounds), its behavior is too erratic for accurately qualifying data in that region. Additionally, incorporating a surrogate compound that elutes earlier in the analysis, and one that encompasses another compound class (1,2-Dichloroethane-d4), should be considered.

Matrix spike compound recoveries exhibited consistent recoveries regardless of external variables (humidity, canister to canister variation) and could add extremely valuable information in the assessment of possible matrix or canister-target compound interactions.

Integration of a spiking protocol into TO-14A and TO-15 could add a significant quality assurance element that analysts and end users could use to validate the accuracy of data generated with this method. The spiking protocol would also enhance the laboratory's ability to troubleshoot their analytical system and evaluate the integrity of the sample canisters.

The procedure detailed here for spiking monitoring compounds into ambient air sampling canisters prior to collection has been shown to be an effective and accurate way of supporting analytical data generated via Method TO-14A and TO-15. Additional work should be done to investigate and identify those compounds for use as monitoring spikes that may add additional improvement in stability, recovery, and relationship to method target compounds.

Acknowledgments

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REFERENCES

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2. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-15, Second Edition*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA 600/625/R-96/010b, January 1997

KEYWORDS

TO-14A, TO-15, Surrogate, Matrix, Spiking, Canister